

IV.F.2 Fuel Processors for PEM Fuel Cells

Levi Thompson

University of Michigan

Department of Chemical Engineering

3026 H.H. Dow Building

Ann Arbor, MI 48109-2136

Phone: (734) 647-7150; Fax: (734) 763-0459; E-mail: ltt@umich.edu

DOE Technology Development Manager: Kathi Epping

Phone: (202) 586-7425; Fax: (202) 586-9811; E-mail: Kathi.Epping@ee.doe.gov

Subcontractors:

Osram Sylvania, Towanda, Pennsylvania

Ricardo, Inc., Plymouth, Michigan

Objectives

- Demonstrate high-performance desulfurizer, catalyst, microreactor and microcombustor/microvaporizer concepts that will enable production of compact fuel processors for polymer electrolyte membrane (PEM) fuel cells.
- Design, fabricate and evaluate a 1 kW_e fuel-flexible (including EPA Phase II reformulated gasoline) fuel processor (during first 36 months).
- Design, fabricate and evaluate a fuel-flexible (including EPA Phase II reformulated gasoline) fuel processor capable of producing up to 10 kW_e hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- I. Fuel Processor Startup/Transient Operation
- J. Durability
- M. Fuel Processor System Integration and Efficiency
- N. Costs

Approach

Tasks devised to accomplish the project objectives include:

- Design and model components and systems that would meet power density targets.
- Develop high-capacity sorbents capable of removing sulfur to target levels.
- Develop better-performing autothermal reforming (ATR), water gas shift (WGS) and preferential oxidation (PrOx) catalysts and associated microreactors.
- Fabricate highly efficient microcombustors/microvaporizers.
- Fabricate microchannel reactors and system.
- Evaluate components and fuel processing system.
- Estimate cost for fuel processor.

Accomplishments

- Demonstrated adsorber prototype containing high-capacity sulfur sorbents that significantly out-performed other available sorbents.
- Demonstrated prototype fuel and water microcombustors/microvaporizers.
- Demonstrated ATR, WGS and PrOx prototype reactors containing high-performance catalysts that out-performed available commercial catalysts.
- Assembled breadboard fuel processor.
- Designed fully integrated fuel processor system.

Future Directions

- During this coming year, our goal is to fabricate a fully integrated fuel processor system based on the know-how and components developed thus far.

Introduction

Fuel cells are being developed to power cleaner, more fuel-efficient automobiles. One fuel cell technology under consideration by many automobile manufacturers is polymer electrolyte membrane (PEM) cells operating with H₂ from liquid fuels like gasoline and diesel. A key challenge to the commercialization of PEM fuel cell based powertrains is the lack of sufficiently small and inexpensive fuel processors. Improving the performance and cost of the fuel processor will require the development of better-performing catalysts, new reactor designs and better integration of the various fuel processing components. These components and systems could also find use in natural gas fuel processing for stationary, distributed generation applications.

Approach

Prototype gasoline fuel processors will be produced and evaluated against the Department of Energy technical targets. Significant improvements over the present state-of-the-art will be achieved by integrating low-cost microchannel systems, high-activity catalysts, π -complexation sorbents, and high-efficiency microcombustors/microvaporizers being developed at the University of Michigan. The microchannel system will allow (1) more efficient thermal coupling of the fuel processor operations, thereby minimizing heat exchanger requirements; (2) improved catalyst performance due to optimal reactor temperature profiles and increased heat and

mass transport rates; and (3) better cold-start and transient responses.

The project will be accomplished in three phases. The Phase I effort will focus on demonstrating compact desulfurizer, microreactor and microcombustor/microvaporizer components for a 1 kW_e fuel processor and developing low-cost methods for the production of microchannel systems. The components will provide the basis for design and fabrication of an integrated 1 kW_e ethanol or gasoline fuel processor during Phase II.

Results

Sulfur Adsorber Prototype. Figure 1 shows desulfurization breakthrough curves for fresh and regenerated Ni(II)-Y (SSIE-500) and Ce(IV)-Y zeolites. These sorbents were regenerated via calcination in dry air at 350 and 450°C for 6 hours. The Ni(II)-Y (SSIE-500) had a higher capacity and was more regenerable than the Ce(IV)-Y sorbent. The breakthrough and saturation capacities for these sorbents were 5.1 and 9.3, and 0.4 and 3.9 mg S per gram of zeolite, respectively. The poor regenerability could be due to strong interactions of cerium ions with the adsorbed organosulfur or, more likely, poor zeolitic framework stability with Ce cations. It has been reported that Ce-Y zeolites lose crystallinity after calcination processes.

Microcombustor/Microvaporizer Prototype. A flash-based water/octane vaporizer was designed and fabricated to mate with our existing catalytic

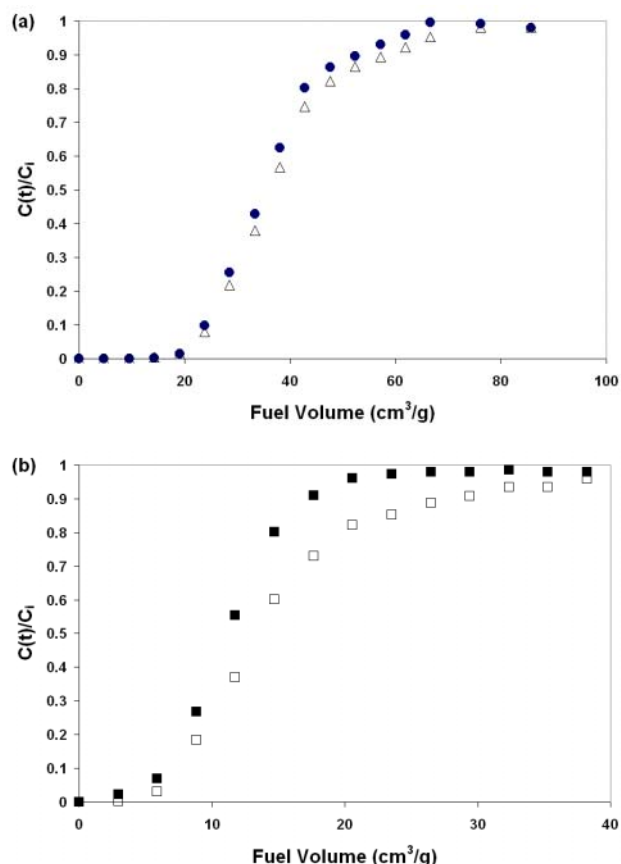


Figure 1. (a) Breakthrough of total sulfur in a fixed-bed adsorber with fresh (Δ) or regenerated (\bullet) Ni(II)-Y (SSIE-500) adsorbents, with diesel feed (297.2 ppmw S) at room temperature. Adsorbent was regenerated in air at 350°C. (b) Breakthrough of total sulfur in a fixed-bed adsorber with fresh (\square) or regenerated (\blacksquare) Ce(IV)-Y (LPIE-80) adsorbents, with diesel feed at room temperature. Adsorbent was regenerated in air at 450°C.

tailgas burner for comparative testing. The flash-based unit is designed to operate at elevated liquid pressures (nominally 10 atm) to maintain water or octane in the liquid phase throughout the heat exchanger coupled to the catalytic tailgas burner. This has the advantage of improving heat transfer from the combustor to the liquid; the low-pressure system was shown in our previous testing to lead to multiphase flow in the heat exchanger. The efficiency is approximately constant with liquid flow rate with the catalytic burner operating on 10% H_2 , indicating that the vaporizer performance is largely independent of liquid flow rate. Essentially the same

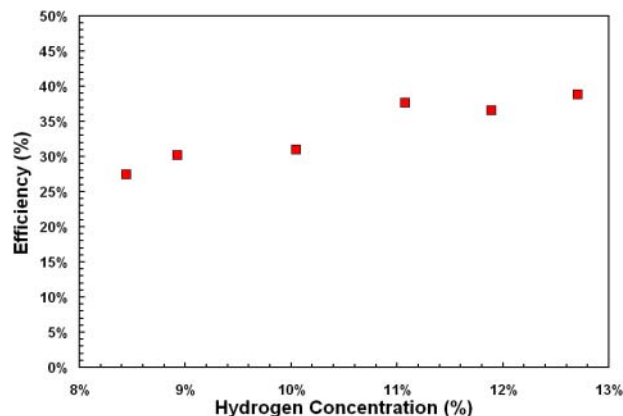


Figure 2. Single-Sided Heat Transfer Efficiency vs. H_2 Concentration in Tailgas Feed to Catalytic Burner

flow rate-independent performance was observed at lower H_2 concentrations. Figure 2 indicates a small increase in heat transfer efficiency with increasing H_2 concentration in the tailgas stream feeding the catalytic burner. This reflects the overall higher temperature at which the system operates with increasing H_2 concentration.

Reactor Prototypes. Individual microreactors containing novel, high-performance ATR, WGS and PrOx catalysts were fabricated. Catalysts in the microreactors were supported on FeCrAlY metal foams (80 ppi). These foams allowed high catalyst loadings, low pressure drop and high thermal conductivities. Each microreactor system was designed to be used to deliver 100 W_e .

The ATR microreactor incorporated 10 foam cores (4 cc) containing 1.5 g of a 10 wt% Ni/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalyst. Figure 3 illustrates the overall conversion (X) and product concentrations for a reactant stream containing iso-octane (0.6 mL/min), air (1.5 L/min) and H_2O (1.1 mL/min). The catalyst was reduced in 5% H_2 prior to the reaction. The power density based on the foams was estimated to be 25,000 W/L versus a target for the ATR of 10,417 W/L. The WGS microreactor incorporated a total of 35 foam cores (14 cc) containing 10.5 g of a 10 wt% Au/ CeO_2 catalyst. Figure 4 illustrates the performance of single- and dual-stage reactor systems for a reactant stream containing 10% CO, 31% H_2O , 6% CO_2 , 39% H_2 and 15% N_2 flowing at 3.75 L/min. The single-stage reactor system

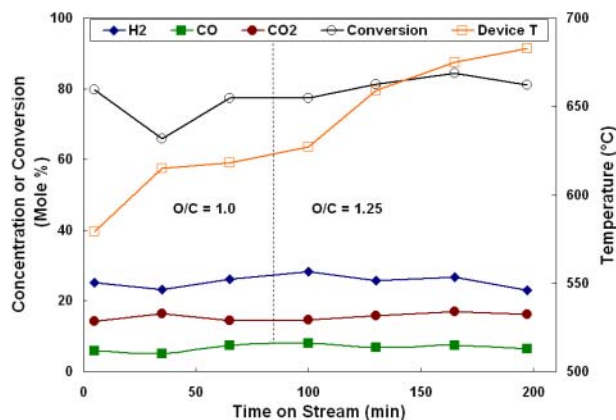


Figure 3. Performance of ATR Microreactor Operating with O/C Ratios of 1.0 and 1.25, and H₂O/C Ratio of 2.0 (The catalyst was reduced in 5% H₂ prior to the rate measurements.)

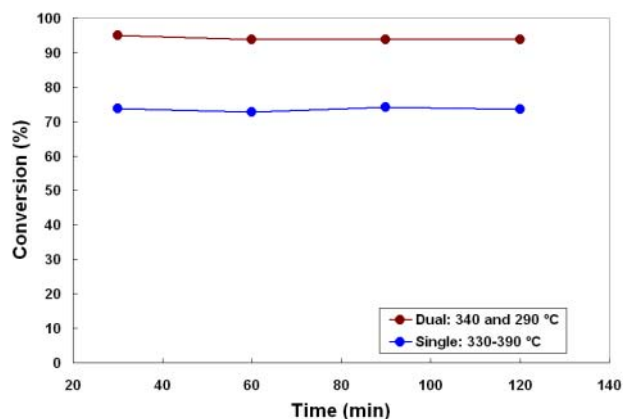


Figure 4. Performance of Single- and Dual-Stage WGS Microreactor Systems (The reactant stream contained 10% CO, 31% H₂O, 6% CO₂, 39% H₂ and 15% N₂ flowing at 3.75 L/min.)

contained 35 channels and was operated at 330-390°C, while reactors in the dual-stage system contained 20 and 15 channels for high- and low-temperature stages that were operated at 340 and 290°C, respectively. The power density based on the foams was estimated to be 7,142 W/L versus a target for the WGS of 2,525 W/L. The PrOx microreactor incorporated 30 foam cores (12 cc) containing 2.4 g of a 4% Pt/Al₂O₃ sol-gel-derived catalyst. Figure 5 illustrates conversions and selectivities for a reactant stream containing approximately 0.8% CO, 0.9% O₂, 15% CO₂, 31% H₂, 15% H₂O and balance N₂, at a space velocity of 50 L/h•g_{cat} and temperature of

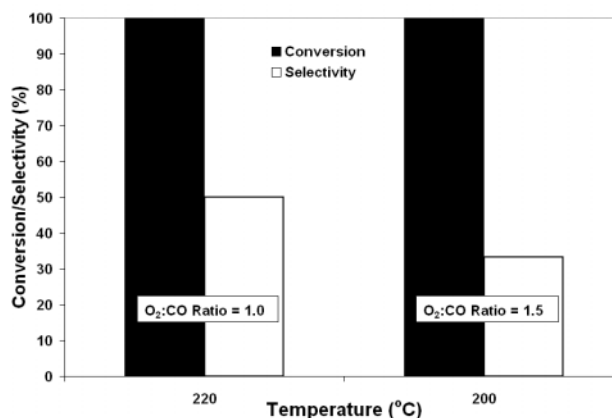


Figure 5. Performance of PrOx Microreactor System Operating at 150°C (The reactant contained 0.8% CO, 0.9% O₂, 15% CO₂, 31% H₂, 15% H₂O and balance N₂.)

150°C. For a two-stage system with half of the catalyst in each reactor, 80% of the air supplied to the first reactor and reactors operating at 200 and 140°C, CO in the reformate was reduced to approximately 5 ppm. The power density based on the foams was estimated to be 8,333 W/L versus a target for the PrOx of 9,091 W/L.

Breadboard Fuel Processor. Schematics of the microreactor core and 100 W_e breadboard fuel processor system are illustrated in Figure 6. Preliminary results are promising and will be verified during the coming year. Performance for this system will be compared to the DOE targets.

Conclusions

Significant progress was made last year. Prototype devices were demonstrated, and their performance exceeded targets established at the beginning of the project. Efforts for the coming year will focus on fabricating an integrated gasoline fuel processor with characteristics that exceed key Department of Energy performance targets.

FY 2004 Publications/Presentations

1. A. J. Hernández-Maldonado and R. T. Yang, "Desulfurization of Commercial Liquid Fuels by Selective Adsorption via π -Complexation

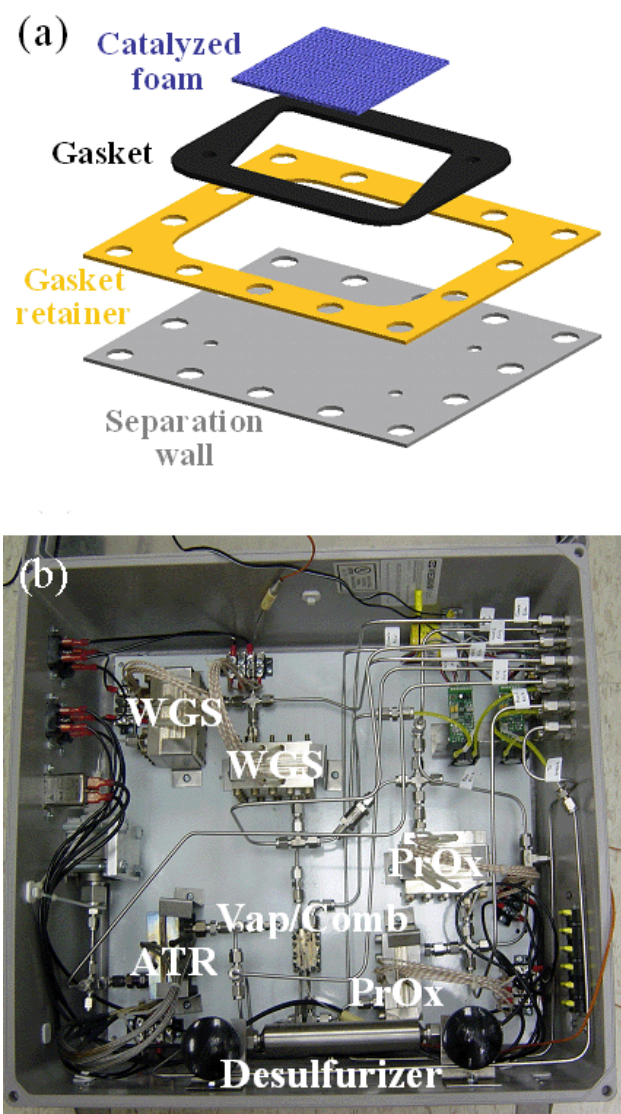


Figure 6. (a) Schematic Illustration of Microreactor Core and (b) Photograph of the 100-W_e Breadboard Fuel Processor System with Insulation Removed

- with Cu(I)-Y Zeolite,” *Ind. Eng. Chem. Res.* **42**, 3103 (2003).
2. R. T. Yang, A. J. Hernandez-Maldonado and F. H. Yang, “Desulfurization of Transportation Fuels with Zeolites Under Ambient Conditions,” *Science* **301**, 79 (2003).
 3. A. J. Hernandez-Maldonado and R. T. Yang, “Desulfurization of Diesel Fuels via π -Complexation with Nickel (II)-Exchanged X- and Y-Zeolites,” *Ind. Eng. Chem. Res.* **43**, 1081 (2004).
 4. A. J. Hernandez-Maldonado and R. T. Yang, “Desulfurization of Diesel Fuels by Adsorption via π -Complexation with Vapor Phase Exchanged (VPIE) Cu(I)-Y Zeolites,” *J. Amer. Chem. Soc.* **126**, 992 (2004).
 5. A. J. Hernandez-Maldonado and R. T. Yang, “New Sorbents for Desulfurization by Selective Adsorption via π -Complexation: Sulfur Removal from Diesel Fuels,” *AIChE Journal* **50**, 791 (2004).
 6. R. T. Yang, “Desulfurization of Transportation Fuels by π -Complexation Sorbents,” Plenary Lecture at the 8th International Conference on Fundamentals of Adsorption (FOA 8), Sedona, Arizona, May 22-28, 2004.
 7. S. Srinivas, A. Dhingra, H. Im and E. Gulari, “A Scalable Silicon Microreactor for Preferential CO Oxidation: Performance Comparison with a Tubular Packed-Bed Microreactor,” *In Press* (on-line August 2004).
 8. Y-W. Lee and E. Gulari, “Improved Performance of NO_x Reduction by H₂ and CO over a Pd/Al₂O₃ Catalyst at Low Temperatures Under Lean-Burn Conditions,” *Catalysis Communications* **5**, 499 (2004).
 9. J. C. Brown and E. Gulari, “Hydrogen Production from Methanol Decomposition over Pt/Al₂O₃ and Ceria Promoted Pt/Al₂O₃ Catalysts,” *Catalysis Communications* **5**, 431 (2004).
 10. C. H. Kim and L. T. Thompson, “Deactivation of Au/CeO_x Water Gas Shift Catalysts,” *J. Catal.*, *accepted* (2004).
 11. C. H. Kim and L. T. Thompson, “Deactivation and Regeneration of Nanocrystalline Gold WGS Catalysts,” North American Catalysis Society Meeting, Cancun, June 2003.
 12. C. H. Kim and L. T. Thompson, “Deactivation and Regeneration of Nanocrystalline Gold WGS

- Catalysts,” Gold Conference 2003, Vancouver, September 2003.
13. C. H. Kim and L. T. Thompson, “Surface Chemistry of Ceria-Supported Gold Water Gas Shift Catalysts,” 7th Natural Gas Conversion Symposium, June 6-10, 2004.
 14. J. Patt, S. Bej and L. Thompson, “Carbide- and Nitride-Based Fuel Processing Catalysts,” 7th Natural Gas Conversion Symposium, June 6-10, 2004.
 15. L. Thompson, “Advances in Catalysis for Hydrogen Production and Fuel Cells,” Georgia Institute of Technology, October 8, 2003.
 16. L. Thompson, “Catalytic Properties of Carbides and Nitrides,” Wilhelm Symposium Honoring B.C. Gates, American Institute of Chemical Engineers National Meeting, November 17, 2003.
 17. A. Tadd, B. Gould, and J. Schwank, “Autothermal Reforming of Iso-octane and Simulated Gasoline Using Nickel-Based Catalysts,” 2003 Annual Meeting Conference Proceedings, Paper 539B, AIChE 2003.
 18. A. Tadd, V. Saraf, J. Schwank, T. Jundee, and T. Rirksomboon, “Supported Nickel Catalysts for Autothermal Reforming of Hydrocarbons,” 18th North American Catalysis Society Meeting, June 1-6, 2003, Cancun, Mexico.
 19. J. Schwank, A. Tadd, and V. Saraf, “High-Throughput Evaluation of Novel Autothermal Reforming Catalysts for Fuel Cell Applications,” EuropaCat VI, August 31-September 4, 2003, Innsbruck, Austria.